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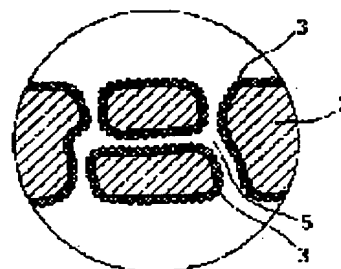
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## (54) DIESEL EXHAUST GAS PURIFYING FILTER AND PRODUCTION THEREOF

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a diesel exhaust gas purifying filter low in pressure loss and having material with a large surface area such as an activated alumina, deposited on the surface and the inside part of a honeycomb cell side wall.

**SOLUTION:** The filter has a porous ceramic filter constituted so as to collect particulates contained in the exhaust gas on the surface and the inside part of the cell side wall 2 by alternately sealing both ends of the cell opening part of a ceramic honeycomb structural body to make the exhaust gas to flow to the adjacent cell through pores of the cell side wall 2 of the honeycomb. In such a case, the cell wall of the honeycomb structural body has 40-60% porosity and 5-35 $\mu$ m average pore diameter and is coated with a slurry containing the activated alumina having smaller particle diameter than the average pore diameter.



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CLAIMS

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[Claim(s)]

[Claim 1] Exhaust gas in the cel which passes the pore of the cel side attachment wall of a honeycomb, and adjoins by \*\*\*\*\* (ing) the both ends of cel opening of a ceramic honeycomb structure object by turns A sink, It has the porosity ceramic filter which was made to carry out uptake only of the particulate contained in exhaust gas a front face and inside the cel side attachment wall. In the diesel emission-gas-purification filter which supported the catalyst metal which burns said particulate to said side-attachment-wall front face and interior the porosity of the cel side attachment wall at 40 - 65% [ said ceramic honeycomb structure object ] The diesel emission-gas-purification filter characterized by supporting the high specific-surface-area ingredient with which the thing of a particle size smaller than the average pore size occupies more than 90wt% as support which average pore size is 5-35 micrometers, and supports said catalyst metal.

[Claim 2] The filter according to claim 1 with which the catalyst metal which consists of at least one kind of platinum group metals is supported.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention removes a particulate at least among the matter contained in the gas discharged by internal combustion engines, such as a diesel power plant, and relates to the filter for particulate uptake used in order to purify the hydrocarbon in exhaust gas (HC), and a carbon monoxide.

[0002]

[Description of the Prior Art] The matter harmful to the body is contained in the particulate discharged by internal combustion engines, such as a diesel power plant, and it has been a technical problem on an environment to remove this. For this reason, in the former, after it carries out uptake of the particulate and it carries out constant-rate uptake with the filter prepared in the exhaust air system of a diesel power plant, the approach of carrying out combustion removal of the particulate by the electric heater, a burner, etc. is performed. Moreover, the combustion temperature of a particulate [ the platinum metal catalyst supported in the filter ] is lowered, and there is also a method of burning continuously the particulate which carried out uptake. In the case of the approach of carrying out combustion removal of the particulate in which the former carried out uptake by the electric heater, a burner, etc., the filter maximum temperature at the time of combustion rises, so that there are many particulate amounts of uptake, a filter may be damaged with the thermal stress concerning a filter, and the particulate amount control of uptake is important, and it has come to control the amount of uptake completely. Since the thermal stress which combustion temperature becomes comparatively low and is applied to a filter becomes small in combustion by the latter catalyst, it excels in thermal resistance.

[0003] Generally in the above-mentioned approach, the cordierite which shows low-thermal expansibility is mainly used for particulate uptake as the quality of the material, using the honeycomb structure object of a ceramic in many cases.

[0004] Cel opening of one end of the ceramic monolith of honeycomb structure, for example, cel opening by the side of a gas inlet, is \*\*\*\*\*(ed) for the diesel emission-gas-purification filter made into the object of this invention every piece, and cel opening by the side of a gas outlet is chisel \*\*\*\*\*(ed) about the cel which opening of an entrance side is not \*\*\*\*\*(ing). Therefore, exhaust gas passes the pore of a cel side attachment wall, and uptake of the particulate which flows with exhaust gas is carried out inside the front face of this cel rule wall, and the pore of a cel rule wall.

[0005]

[Problem(s) to be Solved by the Invention] When the porosity ceramic filter of honeycomb structure \*\*\*\*\* the both ends of a monolith honeycomb by turns as mentioned above, gas has an advantage with particulate collection efficiency higher than the filter of other structures for the structure of flowing in the cel which passes the several micrometers - dozens of micrometers pore of a cell wall, and adjoins. In order to support a catalyst in this filter, when coating the interior of a cel side-attachment-wall front face and the pore of a cel side attachment wall with high specific-surface-area ingredients, such as an activated alumina, as that support, there is a problem that pressure loss becomes high compared with the filter which a high specific-surface-area ingredient blockades the pore of a cel side attachment wall, and has not coated. Since it will lead to the fall of engine power if the pressure loss of a filter is high, the lower possible one of pressure loss is good. However, in order to make pressure loss low, when the porosity of a filter and a pore diameter are enlarged too much, there is a possibility of reducing particulate collection efficiency.

[0006] When coating the ceramic support of honeycomb structure with high specific-surface-area ingredients, such as an activated alumina, some things which specified the particle size of an activated alumina are well-known. Although it has prescribed that activated-alumina particle size is 0.1-100

micrometers by JP,55-1818,B, mixing with amorphous aluminas, such as boehmite, is a premise, and it is supposed that the bond strength of an activated-alumina coating layer will improve by this. Moreover, in JP,4-80736,B, it is supposed by prescribing that the mean particle diameter of an activated alumina is 20 micrometers or less that it is effective in securing the dispersibility by which the activated-alumina slurry was stabilized, and the bond strength of an activated-alumina coating layer will improve. However, when the ceramic support of honeycomb structure is coated with an activated alumina, all are aimed at raising bond strength in order to prevent exfoliation of a coating layer. And these are flow through mold exhaust gas purges, in order not to pass through the inside of the wall of a honeycomb, for exhaust gas to be the thing of a format which passes through the tubular path formed with the wall, to be unable to call it a filter and to strengthen reinforcement of a wall, generally, the porosity of a wall is low and a pore diameter is small.

[0007] By \*\*\*\*\* (ing) the both ends of the porosity monolith honeycomb of honeycomb structure by turns, in the porosity honeycomb filter of structure which flows in the cell which gas passes the pore of a cell wall and adjoins, this invention coats homogeneity with charges of high facing, such as an activated alumina, not only the front face of a cell side attachment wall but inside the pore of a cell side attachment wall, and aims at offering what moreover does not produce the problem that pressure loss is high.

[0008]

[Means for Solving the Problem] In the diesel emission-gas-purification filter which has a porosity ceramic honeycomb structure object according to invention according to claim 1 the porosity of the cell side attachment wall of this honeycomb structure object at 40 - 65% When more than 90wt% of the high specific-surface-area ingredient which average pore size is 5-35 micrometers, and is supported by this makes it smaller than the average pore size of the above-mentioned honeycomb structure object cell side attachment wall The diesel emission-gas-purification filter which has coating of the high specific surface ingredient of this invention can be made [ of pressure loss ] low.

[0009]

[Embodiment of the Invention] The diesel emission-gas-purification filter of this invention covers high specific-surface-area ingredients, such as an activated alumina, on the cell side-attachment-wall front face of a ceramic monolith honeycomb structure object, and the interior pore front face of a cell side attachment wall, covers a catalyst metal on it, and is made by \*\*\*\*\* (ing) by turns the both ends of cell opening of the honeycomb subsequently obtained.

[0010] The ceramic monolith honeycomb structure object used for this invention It is desirable to be made from the cordierite (chemical composition  $2\text{MgO}$ ,  $2\text{Aluminum}_2\text{O}_3$ , and  $5\text{SiO}_2$ ) conventionally known as low-thermal expansion coefficient ceramics. It is about 45% - 60% preferably [ the porosity of a side attachment wall / that it is about 40% - 65% ], and more preferably, and is about 10 micrometers - 30 micrometers preferably [ average pore size / that it is about 5 micrometers - 35 micrometers ] and more preferably.

[0011] As for the particle size of high specific-surface-area ingredients, such as an activated alumina with which said honeycomb structure object is coated on the other hand, it is desirable that they are more than the 90wt% and a desirable particle size more than with 95wt% smaller than the average pore size of said honeycomb structure object. When there is more what has a larger particle size of a high specific-surface-area ingredient than the average pore size of said honeycomb structure object than 10wt(s)%, since do not go into the pore inside the cell side attachment wall of said honeycomb structure object, but a wrap quantity specific-surface-area ingredient increases a cell side-attachment-wall front face relatively, the thickness of a coating layer becomes thick and a pressure drop buildup becomes large, a high specific surface ingredient is not desirable. Moreover, when the particle size of the thing beyond 90wt% of a high specific-surface-area ingredient is smaller than the average pore size of said honeycomb structure object, the high specific-surface-area ingredient included in the pore inside a cell side attachment wall increases. The rise of a pressure loss can be suppressed by distributing homogeneity and coating, without performing the Ayr blow or suction with a cleaner enough at this time, removing the excessive charge slurry of high facing, and making the inside of pore blockade. When a pressure loss makes Ayr flow in a filter from the entrance side of a filter and makes Ayr flow out of a filter from the outlet side of a filter, the amount of Ayr which is the difference of Ayr of an entrance side and an outlet side, and is made to flow from an entrance side is measured the condition for 2000L/(linear velocity of 1.8cm/second), and it is desirable that it is below 45mmAq (water column).

[0012] The cell of an outlet side is discharged from the outlet of a cell where the gas which flowed from the cell of an entrance side as structure for the diesel emission-gas-purification filter of this invention to carry

out uptake of the particulate contained in the exhaust gas of a diesel power plant passes through a cel side attachment wall for a \*\*\*\*\* suggestion \*\*\*\*\* reason, and adjoins. When passing through a cell wall, uptake only of the particulate in exhaust gas is carried out. When smaller at this time than the range of the above [ the porosity and average pore size of a honeycomb before activated-alumina covering which constitutes a filter ], particulate collection efficiency improves, but since the pressure loss of a filter becomes high and engine power declines, it is not desirable. Moreover, since particulate collection efficiency will fall if larger than this range, it is not desirable.

[0013] Moreover, the reason the particle diameter of high specific-surface-area ingredients, such as an activated alumina, is the above range is because a high specific-surface-area ingredient needs to trespass upon the interior of the pore of the cel side attachment wall of said honeycomb structure object. Although only the front face of a cel side attachment wall coated honeycomb mold monolith support with the high specific-surface-area ingredient conventionally, since the particulate contained in exhaust gas stops on the front face of the cel side attachment wall of a filter, and at the interior of the pore of a cel side attachment wall in the case of the honeycomb mold filter of the structure where exhaust gas passes through the interior of pore of a cel side attachment wall, a particulate needs to contact inside this high specific-surface-area ingredient and pore at this time in order to receive a catalysis. Therefore, the aforementioned particle size is required for a high specific-surface-area ingredient. Moreover, the amount of coats of said high specific-surface-area ingredient (the amount of support) has desirable 20 - 75 g/L. When there are few amounts of coats than 20 g/L, the purification capacity of exhaust gas is not low desirable. Moreover, when larger than 75 g/L, since the pressure loss of a filter becomes high and engine power declines, it is not desirable.

[0014] As a high specific-surface-area ingredient in this invention, the other silicas of an activated alumina, a zirconia, a titania, or the thing containing two or more of sorts of these can be used.

[0015] The diesel emission-gas-purification filter of this invention carries out uptake of the particulate contained in the exhaust gas of a diesel power plant at least, and carries out combustion removal. A filter is coated with high specific-surface-area matter, such as an activated alumina, for making a platinum group catalyst metal into the support for carrying out coating preferably. Generally, a platinum group catalyst metal is used as a catalyst which lowers a particulate combustion temperature, and is further used as an oxidation catalyst of a carbon monoxide or a hydrocarbon. The filter of this invention is a filter which has supported the metal catalyst which consists of at least one kind of platinum group metals preferably.

[0016] Next, the diesel emission-gas-purification filter of this invention is concretely explained with drawing 1 -3. Like drawing 1 , the porosity ceramic filter of this honeycomb structure forms the coating layer 4 which becomes the cel side attachment wall 2 of a honeycomb mold filter from the activated-alumina particle 3 by \*\*\*\*\* (ing) by turns by the \*\*\*\*\* material 1 of the both ends of a monolith honeycomb. If the activated alumina of a particle size smaller than the average pore size of a filter is used like drawing 2 which expanded the A section of drawing 1 , since coating is carried out without blockading the interior of the pore 5 of a cel side attachment wall, there are few pressure drop buildups of a filter. However, since the pore of a cell wall is made to blockade when the activated alumina of a bigger particle size than the average pore size of a filter is used like drawing 3 which expanded the A section of drawing 1 , the pressure loss of a filter goes up sharply. Moreover, the purification effectiveness of the exhaust gas components (HC, CO, etc.) of a particulate and others by which uptake was carried out to the coating part of an activated alumina inside the cell wall by supporting a platinum group catalyst metal is raised. In addition, the publication of a catalyst metal layer is omitted in these drawings.

[0017] The diesel exhaust gas containing a particulate advances into a cel from the cel entrance side 6, passes a cell wall 2, and leaves it from the cel outlet side 7. At this time, uptake of the particulate is carried out by the pore of a cell wall front face and the interior. Although a platinum group catalyst metal is anew coated after it usually coats an activated alumina, it is also possible to coat with the solution mixed with the activated alumina.

[0018]

[Example] The filter coated using the above ingredients can be suitably used as a diesel particulate filter of low voltage loss. Below, the example and example of a comparison are shown.

[0019] [Example 1] A silica, an aluminum hydroxide, and talc are used for the main raw material. It adds the carbon for adjusting so that it may become a cordierite ( $2\text{MgO}$ ,  $2\text{aluminum}_2\text{O}_3$ , and  $5\text{SiO}_2$ ) presentation, and then making it porosity -- these main raw materials -- receiving -- 20wt(s)% -- Produce a ceramic honeycomb structure object by the well-known extrusion process, and it calcinates by the 1350 degrees C - 1450 degrees C maximum temperature, the 5 \*-200 degree C programming rate, and the holding time of 2 - 20 hours. Porosity had the pore property which is 28 micrometers of average pore size

55%, and the porosity cordierite honeycomb structure object with a diameter [ of 140mm ] and a die length of 130mm 0.45mm in cel side-attachment-wall thickness and whose number of cels per 1 square inch are 150 pieces was acquired.

[0020] On the other hand, as a high specific-surface-area ingredient, with 5 micrometers of diameters of a centriole, the particle with a larger particle size than 28 micrometers mixed and stirred 670g (Sumitomo Chemical make) of activated aluminas not more than 5wt%, and alumina sol (product made from Nissan chemistry) 330g with 4l. of water, and produced the activated-alumina slurry.

[0021] The aforementioned porosity cordierite honeycomb structure object was completely dipped in the activated-alumina slurry (wash coat). Then, the slurry which adhered too much in an air cleaner and compression Ayr was removed as completely as possible. Five kinds of honeycombs from which coating is repeated and the amount of coats differs were produced. Furthermore, after that, it dried at 120 degrees C for 2 hours, and calcinated at 800 degrees C. The amount of coats per unit volume was computed from the honeycomb weight difference before and behind a wash coat <amount [g/L] of coats = (after [ a before / a coat / weight-coat ] weight) / honeycomb volume>. Then, after dipping 0.1 mols into the chloroplatinic acid water solution of /L for 30 minutes and making it dry at 120 degrees C for 2 hours, it calcinated at 800 degrees C and platinum was made to support. The amounts of support of platinum were about 2 g/L.

[0022] Cel opening by the side of the gas inlet of the honeycomb structure object which made platinum support was \*\*\*\*\* (ed) every piece, and it \*\*\*\* (ed) [ chisel ] in the gas outlet side about the cel which is not \*\*\*\*\* (ing) by the entrance side. Especially as long as \*\*\*\*\* material is a ceramic ingredient with the thermal resistance of 1000 degrees C or more, such as cordierite, an alumina, and a zirconia, it may not be limited, but the adhesives made from a ceramic are sufficient as it. Cordierite was used in this example. Thus, the filter with catalyst support with which the amounts of activated-alumina coats differ was produced (support A-1 - support A-4).

[0023] [Example 2] The porosity cordierite honeycomb filter used in the example 1 and the same filter were produced by the same approach, and as a high specific-surface-area ingredient, with 2 micrometers of diameters of a centriole, the bigger particle than 28 micrometers mixed 670g (Sumitomo Chemical make) of 5% or less of activated aluminas with alumina sol (product made from Nissan chemistry) 330g, and 4l. of water, and carried out the wash coat of said filter to the stirred activated-alumina slurry. Five kinds of filters with which coating is repeated and the amounts of coats differ were produced. Then, the slurry which adhered too much in an air cleaner and compression Ayr was removed as completely as possible. Furthermore, after that, it dried at 120 degrees C for 2 hours, and calcinated at 800 degrees C. After having dipped into the chloroplatinic acid water solution for 30 minutes after investigating the amount of coats, and making it dry at 120 degrees C for 2 hours, it calcinated at 800 degrees C and platinum was made to support. The amounts of support of platinum were about 2 g/L.

[0024] Then, cel opening by the side of the gas inlet of the honeycomb structure object which made platinum support was \*\*\*\*\* (ed) every piece using cordierite, in the gas outlet side, it \*\*\*\* (ed) [ chisel ] about the cel which is not \*\*\*\*\* (ing) by the entrance side, and the filter with catalyst support was produced (support B-1 - support B-5).

[0025] [Example 1 of a comparison] The porosity cordierite honeycomb filter used in the example 1 and the same filter were produced by the same approach, as a high specific-surface-area ingredient, 670g (Sumitomo Chemical make) of activated aluminas of 50 micrometers of diameters of a centriole was mixed with alumina sol (product made from Nissan chemistry) 330g, and 4l. of water, and the wash coat of said filter was carried out to the stirred activated-alumina slurry. Then, the slurry which adhered too much in an air cleaner and compression Ayr was removed as completely as possible. Three kinds of filters with which coating is repeated and the amounts of coats differ were produced. Furthermore, after that, it dried at 120 degrees C for 2 hours, and calcinated at 800 degrees C. After computing the amount of coats, 0.1 mols are dipped into the chloroplatinic acid water solution of /L for 30 minutes, after making it dry at 120 degrees C for 2 hours, it calcinated at 800 degrees C and platinum was made to support. The amount of support of platinum was 2 g/L.

[0026] Then, cel opening by the side of the gas inlet of the honeycomb structure object which made platinum support was \*\*\*\*\* (ed) every piece using cordierite, in the gas outlet side, it \*\*\*\* (ed) [ chisel ] about the cel which is not \*\*\*\*\* (ing) by the entrance side, and the filter with catalyst support was produced (support C-1 - support C-3).

[0027] [the example 2 of a comparison] -- the particle produce the porosity cordierite honeycomb filter used in the example 1, and the same filter by the same approach, and bigger at a main particle size of about 25 micrometers as a high specific-surface-area ingredient than 28 micrometers -- 45wt(s)% -- 670g (Sumitomo

Chemical make) of included activated aluminas was mixed with alumina sol (product made from Nissan chemistry) 330g, and 4l. of water, and the wash coat of said filter was carried out to the stirred activated-alumina slurry. Then, the slurry which adhered too much in an air cleaner and compression Ayr was removed as completely as possible. Four kinds of filters with which coating is repeated and the amounts of coats differ were produced. Furthermore, after that, it dried at 120 degrees C for 2 hours, and calcinated at 800 degrees C. After computing the amount of coats, 0.1 mols are dipped into the chloroplatinic acid water solution of /L for 30 minutes, after making it dry at 120 degrees C for 2 hours, it calcinated at 800 degrees C and platinum was made to support. The amounts of support of platinum were about 2 g/L.

[0028] Then, cel opening by the side of the gas inlet of the honeycomb structure object which made platinum support was \*\*\*\*\* (ed) every piece using cordierite, in the gas outlet side, it \*\*\*\* (ed) [ chisel ] about the cel which is not \*\*\*\*\* (ing) by the entrance side, and the filter with catalyst support was produced (support D-1 - support D-4).

[0029] [Example 3 of a comparison] The porosity cordierite honeycomb filter used in the example 1 and the same filter were produced by the same approach, about 2 g/L support of the platinum was carried out similarly, without carrying out coating by the activated alumina, cel opening by the side of the gas inlet of a honeycomb structure object was \*\*\*\*\* (ed) every piece, by the gas outlet side, it \*\*\*\* (ed) [ chisel ] about the cel which is not \*\*\*\*\* (ing) by the entrance side, and the filter with catalyst support was produced (support E).

[0030] The amount of coats of the support produced in the example and the example of a comparison to Table 1 is indicated.

[0031]

[Table 1]

活性アルミナ 中心粒径 ( $\mu\text{m}$ )	5				2				
担体の種類	A - 1	A - 2	A - 3	A - 4	B - 1	B - 2	B - 3	B - 4	B - 5
活性アルミナの コート量 ( g / L )	3 0	6 1	8 8	1 1 8	3 3	6 5	8 8	1 1 5	1 4 5
活性アルミナ 中心粒径 ( $\mu\text{m}$ )	5 0				2 5				なし
担体の種類	C - 1	C - 2	C - 3	D - 1	D - 2	D - 3	D - 4	E	
活性アルミナの コート量 ( g / L )	2 9	5 8	8 9	3 0	6 4	9 2	1 2 3	0	

[0032] (Measurement of the pressure loss of a filter with catalyst support) The differential pressure of a sink, an entrance side, and an outlet side was measured for compression Ayr from the entrance side of a filter about all the filters of the support A obtained by examples 1 and 2 and the examples 1, 2, and 3 of a comparison - Support E. The measurement result of pressure loss is shown in drawing 4 . From this result, this invention article is understood that a pressure loss is lower than the examples 1 and 2 of a comparison which performed coating.

[0033] (Pore distribution measurement of a filter) Pore distribution was measured about all the filters of the support A obtained by examples 1 and 2 and the examples 1, 2, and 3 of a comparison - Support E. The average pore size of support and the relation of the amount of coats of an activated alumina are shown in drawing 5 . If the amount of coats increases, the average pore size of support becomes small. The advantageous average pore size as a diesel clarifying filter of low voltage loss is 5 micrometers - 35 micrometers.

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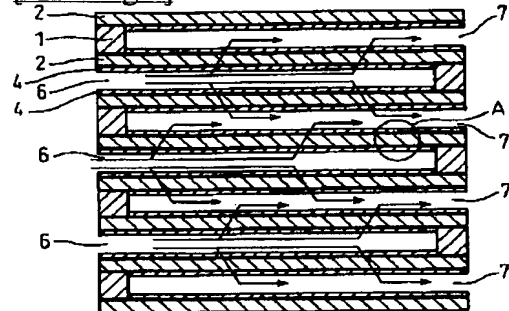
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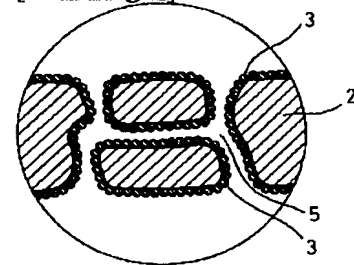
## DRAWINGS

[Drawing 1]

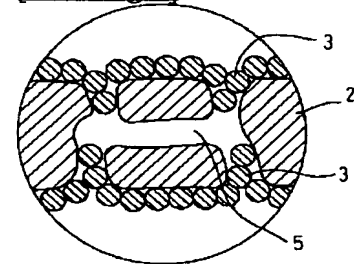


- |                |               |
|----------------|---------------|
| 1 ... 目封じ材     | 5 ... セル側壁の細孔 |
| 2 ... セル側壁     | 6 ... ガス入口側   |
| 3 ... 活性アルミナ粒子 | 7 ... ガス出口側   |
| 4 ... コーティング層  |               |

[Drawing 2]

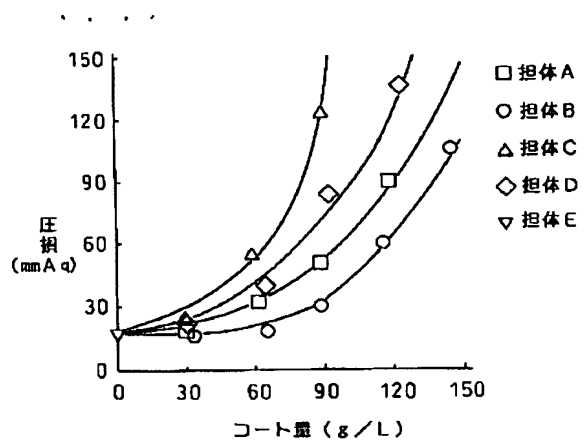


[Drawing 3]

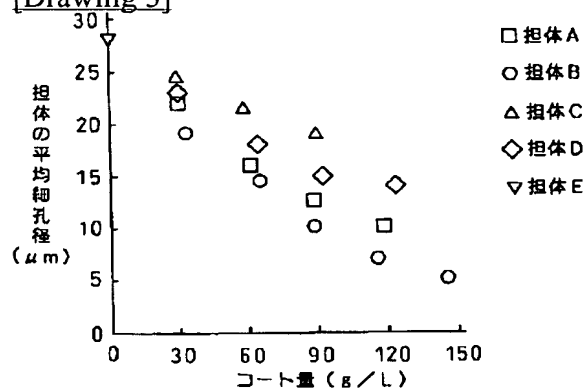


[Drawing 4]





[Drawing 5]



[Translation done.]